DISPLACEMENT REACTIONS OF GRIGNARD REAGENTS IN THE MESITOYLNAPHTHALENES

BY

VICTOR TULLIO

B.S., University of Pennsylvania, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

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Introduction

It is known that diaryl ketones, having a carbonyl group that is obstructed by the presence of such groups as mesityl or duryl from the normal attack of many Grignard reagents, will sometimes undergo attack by these reagents at an atom on the molecule that is removed from the carbonyl group (1). This is exemplified by the displacement of methoxyl groups by the hydrocarbon residue from many Grignard reagents. Compounds such as 2-methoxybenzoylmesitylene and 2,6-dimethoxybenzoyldurene have proved successful in this study.

In order to learn more about the limitations and mechanism of methoxyl displacement, the 2-mesitoylnaphthalene series was chosen since the 1 and 3 positions are not equivalent. In the present work, a study was undertaken of 1,3-dimethoxy-2-mesitoylnaphthalene and related compounds to determine the possible existence of a differential behavior of these *ortho* methoxyl groups toward Grignard reagents.

Hindered ketones in the naphthalene series were also employed for the purpose of investigating further *para*-alkylation reactions that occur in the benzene series through the use of Grignard reagents (2). It was hoped that with compounds such as 1-mesitoylnaphthalene the diminished aromaticity of the naphthalene nucleus would favor the isolation of an intermediate, thus giving an insight as to the mechanism of the formation of *para*-alkylated products.

Discussion

The 1,3-dimethoxy-2-mesitoylnaphthalene was prepared from ethyl 1,3-dihydroxy-2-naphthoate, an Organic Syntheses product (3). Commercially available 3-hydroxy-2-naphthoic

acid was the starting material used in the synthesis of 3-methoxy-2-mesitoylnaphthalene. These two methoxy ketones were treated with several Grignard reagents using different reaction temperatures.

The results of this investigation show that in the 3-methoxy-2-mesitoylnaphthalene series, the 3-methoxyl group is not displaced by the Grignard reagent under any of the conditions which were used. Instead, reaction with the Grignard reagent usually occurs at the 1 position. If this position is occupied by a methoxyl group, displacement occurs; if a hydrogen atom is situated at carbon 1, 1,4-addition occurs. When the 1 position is blocked by an alkyl or aryl radical, no further reaction occurs with the organomagnesium compounds. The unreactivity of the 3-methoxyl group toward Grignard reagents represents the first observed instance of the stability of such a group that is *ortho* to an obstructed carbonyl function. This stability is taken to indicate that *ortho* methoxyl displacement is supressed if the *ortho* carbon atom cannot to any great extent assume a residual positive charge in one of the resonance structures. Thus, another example of the relative unreactivity of the 3 position in 2 substituted naphthalenes toward attacking reagents is added to similar cases already in the literature.

It has been shown that the action of benzylmagnesium chloride on 1-mesitoylnaphthalene yields a dihydro adduct. Although a number of reactions of this type have been realized in the benzene series, this is the first example in which it has been possible to capture the dihydro intermediate. It thus seems clear that these reactions in the benzene series also proceed by way of dihydro intermediates which, under the conditions of the experiments, revert to fully aromatized products.

The action of benzylmagnesium chloride on 4-methoxy-1-mesitoylnaphthalene produces an adduct corresponding to 4-methoxy-2-benzyl-1,2-dihydronaphthalene. Similar adducts have been isolated using the same reagent with 4-methoxy-

benzoylmesitylene and 4-methoxybenzoyldurene (4). These experimental data reveal some similarity of behavior of the phenyl and naphthyl ketones. This similarity evidently disappears when the hydrocarbon residue enters the *para* position.

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VITA

The author was born in Philadelphia, Pennsylvania on May 29, 1927. He attended elementary and high schools in the same city and entered the University of Pennsylvania in September, 1943. After serving in the United States Navy from August, 1945 to August, 1946, he resumed his studies at the University of Pennsylvania and graduated with a Bachelor of Science degree in June, 1948. He entered the Graduate School of the University of Illinois in September of the same year and served as a teaching assistant until June, 1949. He held a University Fellowship from September, 1949 until June, 1950, and was an Allied Chemical and Dye Corporation Fellow in the academic year 1950-51.

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